Experimental diagenesis: Insights into aragonite to calcite transformation of *Arctica islandica* shells by hydrothermal treatment

Laura A. Casella1*, Erika Griesshaber1, Xiaofei Yin1, Andreas Ziegler2, Vasileios Mavromatis3,4, Dirk Müller1, Ann-Christine Ritter5, Dorothee Hippler3, Elizabeth M. Harper6, Martin Dietzel3, Adrian Immenhauser5, Bernd R. Schöne7, Lucia Angiolini8 and Wolfgang W. Schmahl1

1Department of Earth and Environmental Sciences and GeoBioCenter, Ludwig-Maximilians-University Munich, Munich, 80333, Germany
2Central Facility for Electron Microscopy, University of Ulm, Ulm, 89081, Germany
3Institute of Applied Geosciences, Graz University of Technology, Graz, 8010, Austria
4Géosciences Environnement Toulouse (GET), CNRS, Toulouse, 31400, France
5Institute for Geology, Mineralogy and Geophysics, Ruhr-University Bochum, Bochum, 44801, Germany
6Department of Earth Sciences, University of Cambridge, Cambridge, CB2 3EQ, U.K.
7Institute of Geosciences, University of Mainz, Mainz, 55128, Germany
8Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano, Milano 20133, Italy

*Corresponding author: Laura Antonella Casella
Ludwig-Maximilians-University Munich
Department of Earth and Environmental Sciences
Theresienstr. 41
80333 Munich, Germany
Tel.: +49 89 2180-4354
eMail: Laura.Casella@lrz.uni-muenchen.de
Abstract. Biomineralised hard parts form the most important physical fossil record of past environmental conditions. However, living organisms are not in thermodynamic equilibrium with their environment and create local chemical compartments within their bodies where physiologic processes such as biomineralisation take place. Generating their mineralized hard parts most marine invertebrates thus produce metastable aragonite rather than the stable polymorph of CaCO₃, calcite. After death of the organism, the physiological conditions which were present during biomineralisation are not sustained any further and the system moves toward inorganic equilibrium with the surrounding inorganic geological system. Thus, during diagenesis the original biogenic structure of aragonitic tissue disappears and is replaced by inorganic structural features.

In order to understand the diagenetic replacement of biogenic aragonite to non-biogenic calcite, we subjected Arctica islandica mollusc shells to hydrothermal alteration experiments. Experimental conditions were between 100 °C and 175 °C with reaction durations between one and 84 days, and alteration fluids simulating meteoric and burial waters, respectively. Detailed microstructural and geochemical data were collected for samples altered at 100 °C (and at 0.1 MPa pressure) for 28 days and for samples altered at 175 °C (and at 0.9 MPa pressure) for 7 and 84 days, respectively. During hydrothermal alteration at 100 °C for 28 days, most but not all of the biopolymer matrix was destroyed, while shell aragonite and its characteristic microstructure was largely preserved. In all experiments below 175 °C there are no signs of a replacement reaction of shell aragonite to calcite in X-ray diffraction bulk analysis. At 175 °C the replacement reaction started after a dormant time of 4 days, and the original shell microstructure was almost completely overprinted by the aragonite to calcite replacement reaction after 10 days. Newly formed calcite nucleated at locations which were in contact with the fluid, at the shell surface, in the open pore system, and along growth lines. In the experiments with fluids simulating meteoric water, calcite crystals reached sizes up to 200 micrometres, while in the experiments with Mg-containing fluids the calcite crystals reached sizes up to one mm after 7 days of alteration. Aragonite is metastable at all applied conditions. A small bulk thermodynamic driving force exists for the transition to calcite, which is augmented by stresses induced by organic matrix and interface energies related to the nanoparticulate architecture of the biogenic aragonite. We attribute the sluggish replacement reaction to the inhibition of calcite nucleation in the temperature window from ca. 50°C to ca. 170°C, or, additionally, to the presence of magnesium. Correspondingly, in Mg²⁺-bearing solutions the newly formed calcite crystals are larger than in Mg²⁺-free solutions. Overall, the aragonite-calcite transition occurs via an interface-coupled dissolution-reprecipitation mechanism, which preserves morphologies down to the sub-micrometre scale and induces porosity in the newly formed phase. The absence of aragonite replacement by calcite at temperatures lower than 175°C contributes to explain why aragonitic or bimineralc shells and skeletons have a good potential of preservation and a complete fossil record.

Key words. Biominerals, hydrothermal alteration experiments, bivalves, aragonite, calcite, EBSD, EPMA element maps